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Abstract
The asymmetric PS(46k)-b-PMMA(21k) film was spin-coated on a neutral brush layer grafted onto a Spin-On-Glass (SOG) layer on the aluminum oxide layer on a Si substrate. An aluminum oxide layer was used as a hard mask. The PS-b-PMMA film was annealed at 190 degree C under vacuum for 3 days, so that the ~20 nm diameter nanopores in the film was successfully prepared as a result of self-assembly. The nanopores in the PS-b-PMMA film were able to be transferred to the Si substrate by CF4 etching through the SOG and aluminum oxide layers, although the etching was not uniform. The non-uniformity of the etching is also discussed.

Keywords
Nanopore, Self-Assembly, PS-b-PMMA, Membrane, pattern transfer, hard mask, Al2O3

Disciplines
Engineering | Life Sciences | Physical Sciences and Mathematics

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Progress Report II: Fabrication of Nanopores in Silicon Nitride Membrane using Self-Assembly of PS-b-PMMA: Nanopore Pattern Transfer to the Si substrate

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The asymmetric PS(46k)-*b*-PMMA(21k) film was spin-coated on a neutral brush layer grafted onto a Spin-On-Glass (SOG) layer on the aluminum oxide layer on a Si substrate. An aluminum oxide layer was used as a hard mask. The PS-*b*-PMMA film was annealed at 190 °C under vacuum for 3 days, so that the ∼20 nm diameter nanopores in the film was successfully prepared as a result of self-assembly. The nanopores in the PS-*b*-PMMA film were able to be transferred to the Si substrate by CF_4 etching through the SOG and aluminum oxide layers, although the etching was not uniform. The non-uniformity of the etching is also discussed.

Key Words: Nanopore, Self-Assembly, PS-*b*-PMMA, Membrane, pattern transfer, hard mask, Al_2O_3

I. Introduction

Self-assembly of block copolymer (BCP) has attracted attention as an alternative to techniques to fabricate nanoscale features, like e-beam lithography, owing to simplicity in their processing, convenient size, and shape tunability of the structures at the nanoscale by simply changing their molecular weights and compositions.[1–3] However, since the BCP film thickness is ∼60 nm, the maximum etch depth would be in the same range or less, even if the etching selectivity is 1:1. Thus, some hard mask is desirable in the underlayer of the BCP film to overcome this difficulty.

The goal of this project is to fabricate ∼5 nm diameter nanopores in a silicon nitride membrane using self-assembly of BCP poly(styrene-block-methyl methacrylate) (PS-*b*-PMMA), in order to meet potential demand from many applications[4–10] for this process. We previously reported preparation of a membrane of a layered structure of 36.8 μm thick Si and 116 nm thick silicon nitride.[11] In addition, the preliminary result of the self-assembly of asymmetric PS-*b*-PMMA film was also shown. In this report, we describe preparation of a nanoporous film using the self-assembly of PS-*b*-PMMA film, and show nanopore transfer from the BCP film to the Si substrate through a hard mask of aluminum oxide.

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II. Experimental Section

A. Materials

Asymmetric PS-*b*-PMMA (poly-methyl methacrylate rich in syndiotactic contents > 80 %) with the average molecular weight *Mn* of poly-styrene = 46,000, *Mn* of poly-methyl methacrylate = 21,000, and polydispersity index (PDI) =1.09 (polymer domain spacing L_0 = 32 nm) was purchased from Polymer Source, and was used as received. Hydroxyl-terminated random copolymer poly(styrene-*r*-methyl methacrylate),α-hydroxyl-ω-tempo moiety terminated (PS-*r*-PMMA-OH), was also purchased from Polymer Source, and was used as received. The PS content was 60 mol% (*Mn* = 22,500 and PDI = 1.33). Hereafter, PS-*r*-PMMA-OH is referred to as a brush-OH. Spin-On-Glass (SOG, Silicate 15A) was purchased from Filmtronics, and was used as received. CMOS grade toluene (trace impurity level, 10-200 ppb) was purchased from J. T. Baker, and was used as-received as solvent.

B. Aluminum Oxide Deposition

A (100) Si wafer was sonicated in acetone and isopropyl alcohol (IPA) for 5 min each, and was dried using a nitrogen gun. 14 nm thick aluminum oxide film was deposited at 150 °C onto the Si substrate using Cambridge Nanotech S200 Atomic Layer Deposition (ALD). The thickness was determined by Woollam VAS Ellipsometer. The simulation model was Cauchy model.

C. Spin-On-Glass Film Deposition

A SOG film was spin-coated on aluminum oxide film at 3000 rpm for 60 sec, followed by annealing at 80, 150,

and 250 °C for 1 min each on a hot plate to remove the solvent completely and smoothen the surface. The SOG layer was cured at 425 °C for 1 hour in N_2 atmosphere using a Sandvik annealing furnace. The thickness of the SOG layer was determined to be 180.3 nm.

D. Self-assembly of PS-b-PMMA Block Co-polymer

The brush-OH was spin-coated on the SOG layer from 1.1 wt% toluene solution at 2000 rpm for 45 sec. Then, the substrate was baked at 250 °C for 10 min on a hot plate to graft the brush-OH onto the SOG layer. The unreacted brush-OH was removed by sonication in toluene three times for 20 min each. The thickness of the brush layer was determined to be 8.7 nm.

The nanopore self-assembly was separately confirmed to emerge in the 66 to 76 nm thickness on the brush layer on the Si substrate (not shown here). The 69 nm thick PS-*b*-PMMA film was spin coated on the brush layer from the 1.5 wt% toluene solution at 1400 rpm for 45 sec, and was annealed at 190 °C under vacuum for 3 days. The PMMA cylinders were stripped by O_2 plasma etching at 10 sccm at 40 W for 3 min 30 sec using an Anatech Barrel Asher 108. Figure 1 shows an SEM image of the nanopore self-assembly in PS-*b*-PMMA film on the neutral brush layer grafted on the SOG layer on the aluminum oxide layer.

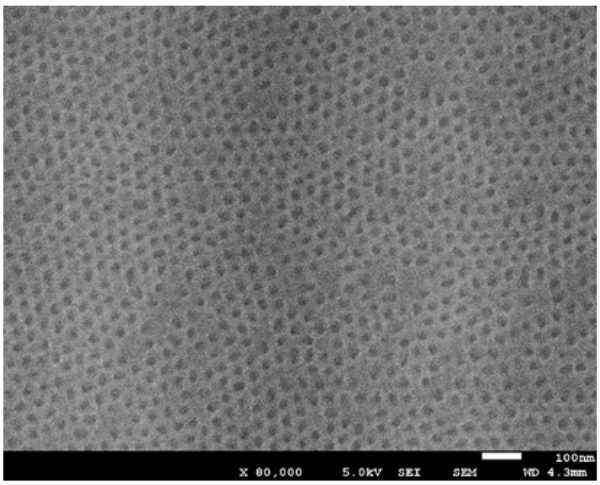

FIG. 1. SEM image of the nanopore self-assembly of PS(46k)-*b*-PMMA(21k) on the neutral brush layergrafted on the SOG layer on the aluminum oxide layer.

E. Pattern Transfer to the Si Substrate

The SOG layer was dry ecthed with the mixed gases of 60 sccm CHF_3 and 2 sccm O_2 at 100 mTorr at 200 W for 2 min 12 sec through the nanopores of the film using an Oxford 80 plus RIE. The aluminum oxide layer was dry etched with the mixed gases of 50 sccm BCl_3 and 5 sccm Ar at 8 mTorr at HF power 40 W at ICP power 1500 W for 14 sec using an Oxford Cobra ICP Etcher. The Si substrate was dry etched with 20 sccm CF_4 at 65 mTorr at 150 W for 1, 2, and 3 min using an Oxford 80 plus RIE. Figure 2 shows the SOG surface after the etching, confirming that the nanopores in the polymer film were transferred to the SOG layer, although the transfer was not uniform.

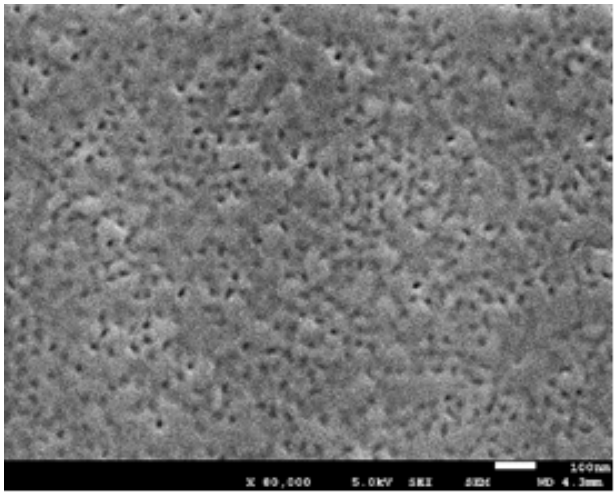

FIG. 2. SEM image of the SOG surface after dry etching.

III. Results and discussion

The Si substrate was etched through the SOG and aluminum oxide layers using the CF_4 dry etching for 1, 2, and 3 min, as described above. All layers on the Si substrate were stripped in 49 wt% HF solution for 1 min after the CF_4 etching. The pattern transfer was confirmed for the sample etched for 3 min, but not for 1 and 2 min. Figure 3 shows an SEM image of the Si surface etched for 3 min.

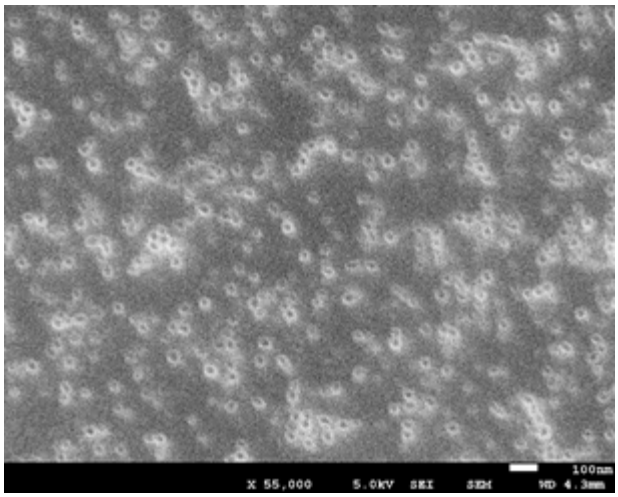

FIG. 3. SEM image of the Si surface after removing all layers from the Si substrate. The Si substrate was etched for 3 min with CF_4 through the SOG and aluminum oxide layers.

The diameters of the nanopores on the Si substrate are

in the range of 20 nm, as can be seen in Fig.3, confirming that the nanopores are transferred onto the Si substrate, although the etching is not uniform. The etching depth of some nanopores is deep, but that of others are shallow, suggesting that the etching depth of the aluminum oxide layer is not uniform. The etch rate of the ALD aluminum oxide in CF_4 plasma was determined to be 2 nm/min. Since the nanopore pattern transfer was not observed for the samples etched for 1 and 2 min, the 4 nm thick aluminum oxide layer should still remain on the Si substrate at least. The non-uniformity of the etching should be ascribed to the residual aluminum oxide layer. The cross-section of the nanopores will be reported soon.

IV. Summary

The 69 nm thick PS(46k)-*b*-PMMA(21k) film was prepared on the neutral brush layer grafted onto the 180 nm thick SOG layer on the 14 nm thick aluminum oxide layer on the Si substrate. The aluminum oxide layer was used as a hard mask. The PS-*b*-PMMA film was annealed at 190 °C in vacuum for 3 days, so that the ∼20 nm diameter nanopores in the film were able to be prepared as a result of the self-assembly. The nanopores in the PS-*b*-PMMA film could be transferred to the Si substrate by CF_4 etching through the SOG and aluminum oxide layers, although the etching was not uniform. The non-uniformity should be ascribed to the residual aluminum oxide layer on the Si substrate.

V. Acknowledgements

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